Atmospheric Chemistry – Chlorine Chemistry

Final report

Tel-Tek report no. 2211030-CC07 v2

Claus Jørgen Nielsen
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Tel-Tek
Kjølnes ring 30
NO-3918 Porsgrunn
NORWAY

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Author(s) Claus Jørgen Nielsen	*Report no.* 2211030-CC07 v2	*Date* 08.11.2011
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Abstract

The present report summarises the findings and conclusions from the *Atmospheric Chemistry – Chlorine Chemistry* project. The project has provided sound scientific data that fill the knowledge gaps relating to amine + chlorine chemistry. The recommendation is that there is no need for further amine + chlorine chemistry studies, and that there is no need to include Cl atom chemistry in dispersion models.

A potentially important gap in the current knowledge has been uncovered: Br atom reactions with amines could be more important than the corresponding Cl atom reactions in the Mongstad area. It is suggested to refine the atmospheric model simulations of halogens in the Mongstad area to obtain a better description of Br atom formation, and to carry out a single kinetic study of the reactions of Br atoms with dimethylamine or trimethylamine.

The project has achieved its targets.

We have reviewed this report and find it in accordance with Tel-Tek's quality system

Project leader: Jon Hovland
Signature:

Department leader: Hans Aksel Haugen
Signature:

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Tel-Tek
Kjølnes Ring 30
NO-3918 Porsgrunn
NORWAY

Telephone:
+47 35 57 40 00
Telefax:
+47 35 57 40 10

E-mail:
tel-tek@tel-tek.no
Web:
www.tel-tek.no

Busines register no.:
NO 943 161 895 MVA

About the Atmospheric Chemistry project

Gassnova has awarded Tel-Tek a contract (no. 257430177) for the project "Atmospheric chemistry". The project has four sub-projects:

- Aqueous phase chemistry
- Nitrosamine photolysis
- Dark chemistry
- Chlorine chemistry

Tel-Tek has entered a consortium agreement with universities and research institutions to carry out the project:

- University of Oslo. Norway
- Leibniz-Institut für Troposphärenforschung. Germany
- Universität Innsbruck. Austria
- IRCELYON. France
- Universidad de Castilla-La Mancha. Spain
- Georgia Tech. USA
- Norwegian University of Life Sciences. Norway

Quality Assurance

The data and results in this report has been quality controlled and verified according to generally accepted principles for publication in internationally recognised scientific journals. This statement also includes the reports within the project that is used as a basis for the conclusions and recommendations in this report.

Claus J. Nielsen
University of Oslo

CONTENTS

1 SCOPE OF SERVICES

The overall objective of the study is to improve the understanding of the chlorine chemistry of amines in the gas phase and provide data for air quality model implementation. The sub goals are stated as:

1. To evaluate the overall status and approach taken to atmospheric chemistry as described in "Basis for the TQP4 call-off 2 Studies on Atmospheric Chemistry, CO_2 Capture Mongstad memo, 2010".
2. To identify any significant topics that are either erroneous or missing
3. To specify the conditions at Mongstad related to chlorine radicals
4. To propose a plan for experimental investigation of the most significant topics within chlorine chemistry
5. To assess chlorine kinetics and yields for nitrosamine and nitramine formation for selected amines
6. To compare the kinetics and products obtained from OH and chlorine
7. To recommend conservative and generic figures for chlorine chemistry representing upper bound nitrosamine and nitramine formation kinetics

2 HSE

The project involved handling of hazardous chemicals and was carried out as required by statutes and regulations.

The Standard Operational Procedure (SOP) in the UiO laboratory is that all compounds under study, including possible degradation products, are treated as potentially carcinogenic unless other information is available. The SOP also includes that all toxic/carcinogenic compounds are handled on vacuum lines. A Safe Job Analysis has been conducted and documented.

The University of Oslo is a Governmental institution that follows HSE rules and regulations according to Norwegian Law. UiO is not required to produce HSE data sheets for compounds synthesized for research purpose. The HSE-manual can be found here:

http://www.kjemi.uio.no/intern/organisasjonsutvikling/hms/hse-manual/

No accidents or near accidents have occurred during the project lifetime.

Tel-Tek has reveiewed the Georgia Institute of Technology, School of Chemistry and Biochemistry Safety Manual. (http://www.chemistry.gatech.edu/safety/Safety%20Manual%20November%202006.pdf) and found it in line with best practice. Safe Job Analysis has been conducted and documented. The atmospheric chemical kinetics and photochemistry laboratory was inspected not long time before this project started by the Georgia Tech Office of Environemental Health and Safety and their suggestions for improvements in safety procedures have been implemented. No accidents or near accidents have occurred since current GA Tech laboratory space was occupied in early 2003.

3 ACTIVITIES

The *Atmospheric Chemistry – Chlorine Chemistry* project comprised 6 activities of which activity 3 was setting up an experiment plan. This activity will not be commented further. The results from the other 5 activities are summarized in the following sections.

3.1 Activity 1: Evaluation of the overall status and approach taken to atmospheric chemistry

The overall status and approach taken to atmospheric chemistry as described in "Basis for the TQP4 call-off 2 Studies on Atmospheric Chemistry, CO_2 Capture Mongstad memo, 2010" has been evaluated (Scope of services, items 1 and 2). The evaluation is presented in the Tel-Tek report no. 2211030-NP01, *Atmospheric Chemistry - Review of atmospheric amine chemistry relevant to Mongstad*.[1]

The report pointed out a number of important topics for which data were missing. The following have special relevance to the *Atmospheric Chemistry – Chlorine Chemistry* project:

1. ***Amine + Cl kinetics****: There are no experimental data available. The reactions are expected to very fast, close to the collision limit, and the Cl reaction may contribute significantly to the amine gas phase photo-oxidation. Kinetic data and information from estimates of the gas phase Cl atom concentration in the Mongstad area are needed to quantify the importance of Cl atom chemistry.*

   There is sparse data concerning the amount of nitrosamines/nitramines that can be formed in the gas phase photo-oxidation of secondary amines. The branching in the initial H-abstraction reaction will differ for OH, Cl and NO_3, but the subsequent reactions of the formed amino radical and the amount of nitramine formed will be the same independent of the initial oxidant. There is no simple and sound way to predict the CH:NH branching ratio in the initial hydrogen abstraction reaction in secondary amines. Should the Cl and NO_3 reactions with primary amines turn out to be important, data for the initial branching ratio will be needed.

2. ***Nitramine + Cl kinetics****: Any additional nitramine loss process may be important to the overall budget. Experimental kinetic data for nitramine + Cl reactions are clearly needed.*

The abovementioned knowledge gaps have been effectively and successfully addressed in the "Atmospheric Chemistry – Chlorine Chemistry"-project.

3.2 Activity 2: Specification of the chlorine atmospheric conditions at Mongstad

A literature and model study to characterize the chlorine atmospheric conditions at Mongstad is presented in the Tel-Tek report no. 2211030-CC02, *Atmospheric Chemistry – Chlorine Chemistry. Halogen Chemistry in the Mongstad Region: Literature Study and Model Simulations*.[2]

The concentrations of reactive halogen species in the Mongstad area was calculated employing the SPACCIM box model.[3] The influence of atmospheric pollution (marine, marine-remote, marine-urban), radiation intensity (summer, winter, dimming due to clouds) and aqueous phase chemistry were examined in sensitivity studies, and the results were compared to literature data. The most representative scenario is found to be a mixed urban-marine air mass, when aqueous phase processes were taken into account in the model.

The output Activity 2 has been used as input to Activities 5 and 6.

Comment: The model results indicate that the Br concentration, peaking at 2×10^4 atoms cm^{-3}, is under predicted by 1 or 2 orders of magnitude. The amine + Br reaction could become important if the reaction is as fast as the amine+Cl reaction.

3.3 Activity 4: Kinetic studies of the reactions of Cl atoms with selected amines and nitramines

The "Atmospheric Chemistry – Chlorine Chemistry"-project involved 2 experimental activities:

- Kinetic studies of the reactions of Cl atoms with methylamine, dimethylamine and trimethylamine.
- Kinetic studies of the reactions of Cl atoms with 4 simple nitramines (CH_3NHNO_2, $CH_3CH_2NHNO_2$, $(CH_3)_2NNO_2$ and $(CH_3CH_2)_2NNO_2$).

The results from these experiments are documented in the Tel-Tek reports no. 2211030-CC04, *Atmospheric Chemistry – Chlorine Chemistry. Kinetic Studies of the Reactions of Cl Atoms with Amines,*[4] *and* no. 2211030-CC03, *Atmospheric Chemistry – Chlorine Chemistry. Kinetic Studies of the Reactions of Cl Atoms with Nitramines.*[5]

The obtained rate coefficients for Cl atom reactions with amines and nitramines are included in Annex 1 (page 12). The Cl atoms reactions with amines and nitramines are almost one order of magnitude faster than the corresponding OH reactions. Since the average Cl atom concentration in general is more than 2 orders of magnitude lower than the average OH concentration, the impact of chlorine chemistry is limited, see Activity 5.

3.4 Activity 5: Box modelling - Comparison of amine+OH and amine+Cl chemistry

The activity is described in the Tel-Tek Report no. 2211030-CC05, *Atmospheric Chemistry – Chlorine Chemistry. Comparison of amine+OH and amine+Cl chemistry.*[6]

Box-model simulations were used to evaluate the atmospheric removal of amines by reaction with Cl atoms *vs*. OH radicals. Amine reaction with OH radicals is clearly the major atmospheric gas phase loss process. In absolute numbers, less than 2 % of the total amine emitted is removed by reaction with Cl atoms in the Mongstad area. It is concluded that it is not necessary to include Cl atom chemistry in dispersion modelling.

3.5 Activity 6: Formation rate data

The obtained experimental data were evaluated and analysed in relation to extending a recently developed structure activity relationship (SAR) for Cl atom reaction with hydrocarbons.[7] This is described in the Tel-Tek Report no. 2211030-CC05, *Atmospheric Chemistry – Chlorine Chemistry. Nitroso- and nitramine formation data.*[8]

SAR parameters can in principle be derived for Cl atom reactions with simple amines. However, it makes little sense to do so since the rate coefficients for reaction are already close to the upper limit for gas phase reactions. It is therefore suggested to use a generic rate coefficient for Cl atom reaction with amines, $k_{\text{Amine+Cl}} = 5\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Although fast, the Cl atom reaction with nitramines is too slow to contribute significantly to the total gas phase nitramine loss. The Cl atom reaction with nitrosamines will not be important under any relevant atmospheric condition.

4 CONCLUSIONS AND RECOMMENDATIONS

The *Atmospheric Chemistry – Chlorine Chemistry* project has supplied scientifically sound data as the basis for addressing severe knowledge gaps relating to dark chemistry in the Mongstad region.

1. Amine + Cl kinetics:
There are now experimental kinetic data available for the Cl atom reaction with amines. There is also simulation data for the Cl atom concentration in the Mongstad area. Although the amine+Cl reactions are fast, the Cl atom concentration is too low in the Mongstad area for Cl-chemistry to be important, it is estimated that less than 2 % of the total amine emitted will be removed by reaction with Cl atoms in the Mongstad area. Consequently, there is no need to determine branching ratios in the initial H-abstraction reaction by Cl. Such a study will be both lengthy and costly. It is suggested to use a worst-case scenario branching, such that all amine+Cl reactions will lead to formation of the amino radical. The subsequent reactions are well known from previous studies, see *e.g.* ADA.[11,12]

Recommendation:	*No need for further studies. No need to include amine+Cl reactions in dispersion modelling.*

2. Nitramine + Cl kinetics:
There are now experimental kinetic data available for the Cl reaction with nitramines. The reactions are fast, but the Cl atom concentration is too low in the Mongstad area for Cl-chemistry to be important.

Recommendation:	*No need for further studies. No need to include nitramine+Cl reactions in dispersion modelling.*

3. Amine + Br kinetics:
Results from the *Atmospheric Chemistry – Chlorine Chemistry* project imply a potentially important gap in the current knowledge: Br atom reactions with amines could be more important than the corresponding Cl atom reactions in the Mongstad area. Model calculations indicate that Br atom concentrations in the Mongstad area could be at least an order of magnitude larger than the Cl atom concentrations. Since the Br and Cl atom reactions are expected to proceed in a similar fashion, *i.e.* via an R_3N^*X adduct, the rate coefficients may be of the same magnitude. There are, however, no experimental data available.

Recommendation:	*It is suggested to refine the atmospheric model calculations to include a better description of Br atom formation, and to carry out a single kinetic study of the reactions of Br atoms with either dimethylamine or trimethylamine.*

5 LITERATURE

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ANNEX 1. EXPERIMENTAL RESULTS

The *Atmospheric Chemistry – Chlorine Chemistry* project has generated kinetic data for Cl atom reaction with 3 amines. The experimental rate constants are compared to the corresponding amine + OH data in Table A1. The experimental results are documented in the Tel-Tek report no. 2211030-CC03, *Atmospheric Chemistry – Chlorine Chemistry. Kinetic Studies of the Reactions of Cl Atoms with Amines*.[4] There are no other kinetic data for amine + Cl reactions in the open literature.

Table A1. Comparison of experimental rate constants at 295-300 K for the reactions of OH radicals and Cl atoms with amines.

Compound	k_{OH} /cm^3 molecule^{-1} s^{-1}	Ref.	k_{Cl} /cm^3 molecule^{-1} s^{-1}	Ref.
CH_3NH_2	$(2.20 \pm 0.22) \times 10^{-11}$	13	$(3.5 \pm 0.6) \times 10^{-10}$	4
	$(1.73 \pm 0.11) \times 10^{-11}$	14		
$(CH_3)_2NH$	$(6.54 \pm 0.66) \times 10^{-11}$	15	$(3.9^{+0.7}_{-0.5}) \times 10^{-10}$	4
	$(6.49 \pm 0.64) \times 10^{-11}$	14		
$(CH_3)_3N$	$(6.09 \pm 0.61) \times 10^{-11}$	15	$(4.2 \pm 0.5) \times 10^{-10}$	4
	$(3.58 \pm 0.22) \times 10^{-11}$	14		

The *Atmospheric chemistry – Dark Chemistry* project has generated kinetic data for NO_3 radical reaction with 4 nitramines. Table A2 compares the new data with existing data for the OH radical reaction with nitramines. The experimental results are documented in the Tel-Tek report no. 2211030-DC03, *Atmospheric Chemistry – Chlorine Chemistry. Kinetic Studies of the Reactions of Cl Atoms with Nitramines*.[5] There are no other data on nitramine + Cl kinetics in the open literature.

Table A2. Comparison of experimental rate coefficients at 296-300 K for the reactions of nitrosamines with OH radicals and Cl atoms.

Compound	k_{OH} /cm^3 molecule^{-1} s^{-1}	Ref.	k_{Cl} /cm^3 molecule^{-1} s^{-1}	Ref.
CH_3NHNO_2 (MNA)	$(7.7 \pm 0.7) \times 10^{-13}$	12	$(9.9 \pm 0.7) \times 10^{-12}$	5
$(CH_3)_2NNO_2$ (DMNA)	$(3.6 \pm 0.5) \times 10^{-12}$	16	$(5.0 \pm 0.4) \times 10^{-11}$	5
	$(3.5 \pm 0.5) \times 10^{-12}$	12		
$CH_3CH_2NHNO_2$ (ENA)	1.0×10^{-11} [a]		$(1.64 \pm 0.11) \times 10^{-11}$	5
$(CH_3CH_2)_2NNO_2$ (DENA)	1.9×10^{-11} [a]		$(5.0 \pm 0.3) \times 10^{-11}$	5

[a] Estimated using the OH-SAR of Kwok and Atkinson, Ref. [17].